

Large thermopower in the antiferromagnetic semiconductor BaMn_2Bi_2

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We report electrical and thermal transport properties of Mn-based material BaMn_2Bi_2 with ThCr_2Si_2 structure. The resistivity of the antiferromagnetic BaMn_2Bi_2 shows a metal-semiconductor transition at ~ 80 K with decreasing temperature. Correspondingly, the thermopower S shows a peak at the same temperature, approaching $150 \mu\text{V/K}$. With increasing temperature S decreases to about $125 \mu\text{V/K}$ at the room temperature. The magnetic field enhances the peak value to $210 \mu\text{V/K}$. The Hall resistivity reveals an abrupt change of the carrier density close to the metal-semiconductor transition temperature.

Thermoelectric materials with high Seebeck coefficient S (thermopower) have been attracting significant attention because of potential applications, particularly in waste heat recovery.^{1–4} High figure of merit ($ZT = \sigma S^2 T / \kappa$, where σ and κ are the electrical and thermal conductivity, respectively) usually requires high thermopower. This raises considerable interest in exploratory synthesis of strongly correlated electron materials. Thermopower represents an electrical current entropy flow and therefore the charge/spin/orbital degrees of freedom might be manipulated for its enhancement, particularly around metal-insulator transitions.^{5–8} For example, giant thermopower and a record high thermoelectric power factor up to $S^2/\rho \sim 2300 \mu\text{W K}^{-2} \text{cm}^{-1}$ was observed in FeSb_2 with narrow energy gaps and correlated bands.^{9–12}

Since the discovery of high temperature superconductivity in layered iron pnictide and iron chalcogenide compounds, the large diversity of the layered transitional metal pnictide compounds have been explored.^{13,14} In particular, doped AM_2Pn_2 ($A = \text{Ca, Sr, Ba or Eu}$, $M = \text{Fe, Mn, Rh or Co}$, and Pn is pnictide or chalcogenide element) with ThCr_2Si_2 (122-type) structure have been thoroughly investigated. Besides Fe-based high temperature superconductivity, high thermopower with metallic conduction was observed.^{15–17} Mn-based AM_2Pn_2 materials usually exhibit magnetic ground states with strong correlations.^{18–20} BaMn_2As_2 and BaMn_2Sb_2 are antiferromagnetic semiconductors due to the strong Hund's coupling and the stability of the half-filled d -shell of the Mn^{+2} ions.^{18,19,21,22} Both were predicted to exhibit large Seebeck coefficient.^{19,21} Therefore, it is of interest to explore thermoelectric properties of isostructural and semiconducting BaMn_2Bi_2 .²³

Here we report electrical and thermal transport properties of Mn-based material BaMn_2Bi_2 with ThCr_2Si_2 structure. The resistivity of the antiferromagnetic BaMn_2Bi_2 shows a metal-semiconductor transition at ~ 80 K with decreasing temperature. Correspondingly, the thermopower S shows a peak at the same temperature and the value approaches $150 \mu\text{V/K}$. With increasing temperature S decreases, but is still about $120 \mu\text{V/K}$ at the room temperature. The magnetic field enhances the peak value to $210 \mu\text{V/K}$. The Hall resistivity reveals

an abrupt change of the carrier density close to the metal-semiconductor transition temperature.

Single crystals of BaMn_2Bi_2 were grown using a high-temperature self-flux method.^{24,25} X-ray diffraction (XRD) data were taken with $\text{Cu K}\alpha$ ($\lambda = 0.15418 \text{ nm}$) radiation of Rigaku Miniflex powder diffractometer. Electrical transport measurements up to 9 T were conducted in Quantum Design PPMS-9 with conventional four-wire method. In the in-plane measurements, the current path was in the ab -plane, whereas magnetic field was parallel to the c -axis. Thermal transport properties were measured in Quantum Design PPMS-9 from 2 K to 350 K using one-heater-two-thermometer method. The direction of heat and electric current transport was along the ab -plane of single grain crystals with magnetic field along the c -axis and perpendicular to the heat/electrical current. The relative error in our measurement was $\frac{\Delta\kappa}{\kappa} \sim 5\%$ and $\frac{\Delta S}{S} \sim 5\%$ based on Ni standard measured under identical conditions.

Fig. 1(a) shows the powder XRD pattern of flux grown BaMn_2Bi_2 crystals, which were fitted by RIETICA software.²⁶ All reflections can be indexed in the $I4/mmm$ space group, and the crystal structure features polyanionic $[\text{Mn}_2\text{Bi}_2]^{2-}$ layers separated by Ba ions (Fig. 1(b)). The crystals are plate-like and the base-plane is ab -plane (inset in Fig. 1(a)). The temperature dependence of the magnetization is shown in Fig. 1(c). The high anisotropy and decreasing magnetization with temperature suggest collinear antiferromagnetic order below room temperature, in agreement with previous result.²³

Fig. 2 shows the temperature dependence of the electric resistivity in the ab -plane ρ , thermopower S and thermal conductivity κ . The resistivity decreases with increasing temperature showing semiconducting behavior up to ~ 70 K. At higher temperatures $\rho(T)$ is metallic (Fig. 2(a)). The thermopower S is $125 \mu\text{V/K}$ at 350 K and remains nearly constant with decreasing temperature down to 150 K. The S shows a peak at ~ 75 K and the peak value is $150 \mu\text{V/K}$. Below that temperature S decreases to zero gradually with decreasing temperature to 2 K (Fig. 2(b)). The thermal conductivity κ shows a phonon peak at about 30 K and the maximum value is about 10 W/K m (Fig. 2(c)). The 9 T magnetic field has small influence on the electric resistivity

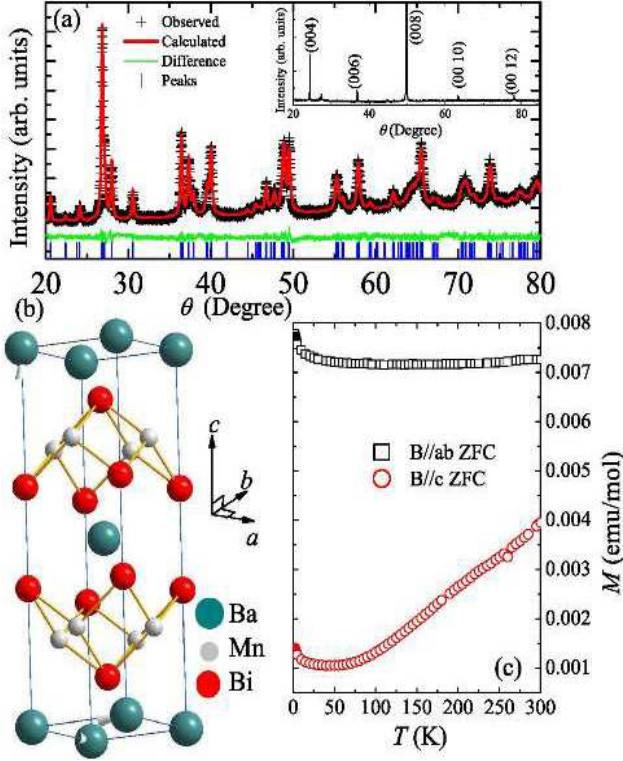


FIG. 1. (a) Powder XRD patterns and structural refinement results. The data were shown by (+), and the fit is given by the red solid line. The difference curve (the green solid line) is offset. The inset is the XRD pattern of single crystal showing the base ab -plane. (b) The crystal structure of BaMn_2Bi_2 . Ba ions are denoted by the largest balls, while Bi and Mn atoms are denoted as the medium and smallest balls respectively. (c) The magnetization of BaMn_2Bi_2 crystal as function of temperature with 1 T magnetic field parallel to ab -plane and c -axis respectively.

and thermal conductivity, but enhances the peak value of the thermopower to $210 \mu\text{V/K}$. The thermopower of BaMn_2Bi_2 is close to the value of typical thermoelectric materials such as PbTe and Bi_2Se_3 , and the thermal conductivity is also small. However, the maximum value of ZT is ~ 0.005 at 300 K due to high electric resistivity. It is reported that K-doping in Ba sites could induce the change of the ground state from semiconductor to metal with significant suppression of the resistivity.²³ But the carrier doping could also decrease the Seebeck coefficient, such as the case in doped FeSb_2 . This could compensate the suppression of the resistivity and make the enhancement of ZT smaller or even impossible. So the thermoelectric properties of K-doped BaMn_2Bi_2 deserve further study.

Fig. 3(a) shows the Hall resistivity ρ_{xy} as a function of the magnetic field B at different temperatures from 5 K to 200 K. In all temperature, the Hall resistivity is

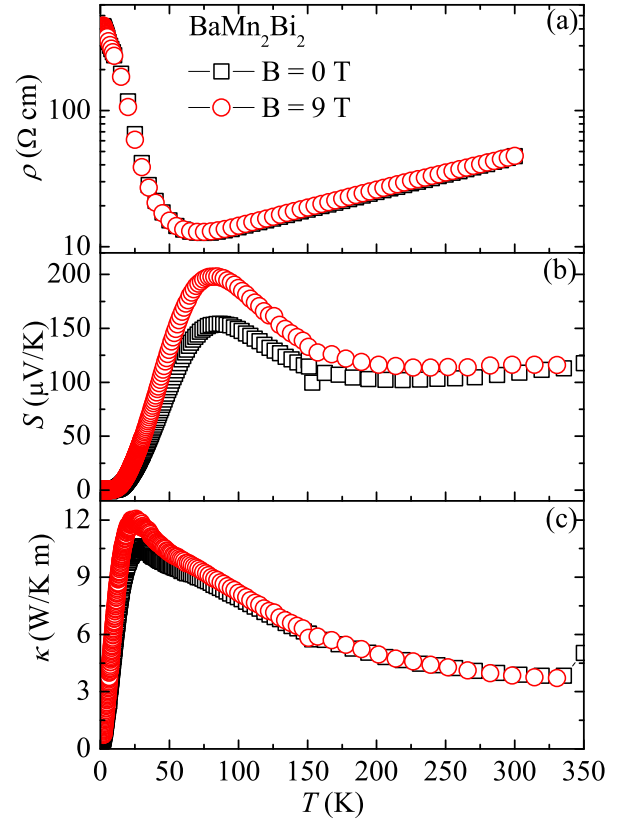


FIG. 2. In-plane resistivity $\rho_{ab}(T)$ (a), Seebeck coefficient $S(T)$ (b) and thermal conductivity $\kappa(T)$ (c) of BaMn_2Bi_2 single crystal as a function of temperature in 0 T and 9 T magnetic field respectively.

positive. This indicates the hole carriers in BaMn_2Bi_2 , consistent with the positive Seebeck coefficient in Fig. 2(b). Besides, the Hall resistivity shows linear field dependence and indicates single-band conduction. In single band semiconductor, the Hall resistivity can be described by single-band Hall resistivity $\rho_{xy} = \frac{B}{n|e|}$ where n is the carrier density and e is the electron charge. The Hall resistivity of BaMn_2Bi_2 can be fitted very well by this formula (the red line in the inset of Fig. 3(b)) and the temperature dependence of the carrier density n derived from the linear fitting is shown in Fig. 3(b).

With increase in temperature, the slope of the Hall resistivity is nearly constant between 5 K and 15 K, and then increases indicating the decrease of the carrier density (Fig. 3(b)). At ~ 40 K, there is a large decrease in the slope of the Hall resistivity and carrier density. This position is close to the semiconductor-metal transition temperature and the peak position of Seebeck coefficient. After that, the carrier density shows a slow increase with increasing temperature.

Seebeck coefficient in a semiconductor is the sum of three different contributions: the diffusion term S_{diff} , the spin-dependent scattering term and the phonon-drag term S_{drag} due to electron-phonon coupling. The diffusion term of a single-band metal always shows lin-

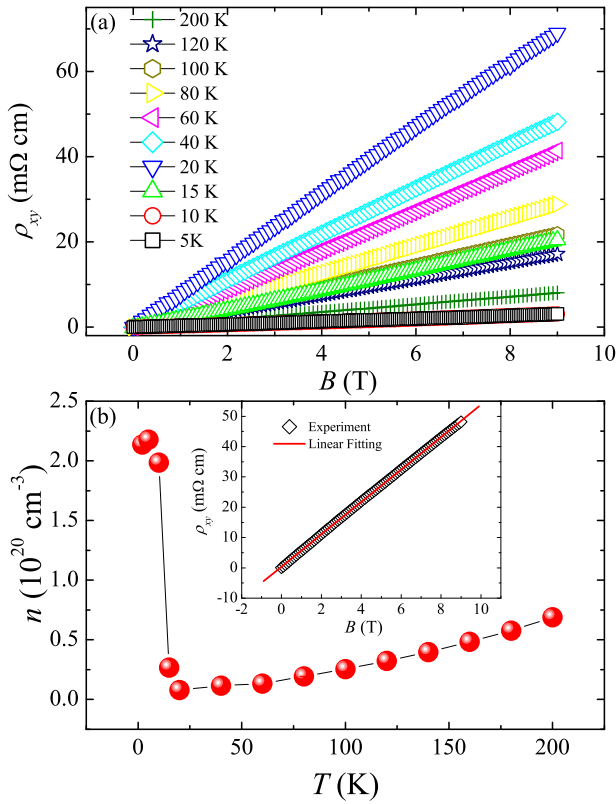


FIG. 3. (Color online) (a) Hall resistivity ρ_{xy} as a function of the magnetic field B at different temperatures. (b) The temperature dependence of the carrier density n deduced from Hall resistivity. The inset shows the linear fitting of the Hall resistivity at 40 K.

ear temperature dependence and the non-monotonic behavior can only come from spin scattering or phonon-drag.^{27,28} In BaMn_2Bi_2 , the magnetic transition temperature (above 400 K) is much higher than the peak position of the Seebeck coefficient and the Seebeck coefficient does not show significant magnetic field dependence except around the metal-semiconductor transition. This indicates the spin-dependent scattering should not dominate the Seebeck coefficient in BaMn_2Bi_2 . The contribution of phonon-drag term gives $\sim T^3$ dependence for $T \ll \Theta_D$, $\sim 1/T$ for $T \geq \Theta_D$ (where Θ_D is the Debye Temperature), and a peak structure for $\sim \frac{\Theta_D}{5}$.²⁸ The Debye temperature of BaMn_2Bi_2 is ~ 150 K.²³ The peak structure from phonon-drag should be at ~ 30 K which is rather different from the observed peak position (~ 75 K) in Fig. 2(b). Hence, the peak of Seebeck coefficient in BaMn_2Bi_2 should not come from the spin-dependent scattering term and the phonon-drag term. Instead, its origin is in the sharp change in the carrier density and the metal-semiconductor transition which is related the strongly correlated effect.

In summary, we report the electronic and thermal transport properties of Mn-based material BaMn_2Bi_2 with ThCr_2Si_2 structure. Thermopower of the antifer-

romagnetic BaMn_2Bi_2 shows a peak at the temperature of the metal-semiconductor transition (~ 80 K) of $150 \mu\text{V/K}$. With increasing temperature S decreases slightly and the value is have $120 \mu\text{V/K}$ at room temperature. The magnetic field enhances the peak value to $210 \mu\text{V/K}$. The Hall resistivity reveals an abrupt change of the carrier density close to the metal-semiconductor transition temperature.

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